Thick YBa$_2$Cu$_3$O$_7$ films by post annealing of the precursor by high rate e-beam deposition on SrTiO$_3$ substrates

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Abstract

High rate evaporation techniques were used to deposit Y, BaF$_2$, and Cu precursor films onto SrTiO$_3$ single crystal substrates at rates in excess of 10 nm/s. Y and Cu were deposited by electron beam (e-beam) heating and thermal heating was used for BaF$_2$. Post deposition annealing was used to form 3 μm thick c-axis aligned YBa$_2$Cu$_3$O$_7$ films on the SrTiO$_3$ substrates. Critical current densities 1.8×10^5 A/cm^2 at 1 T ($H\|c$) and 77 K were achieved. The films were nominally stoichiometric and were post-deposition annealed in a humidified reduced oxygen atmosphere at 725–800°C. These results indicate that the so-called BaF$_2$ post annealing process can be one of several possible candidate methods for production of thick YBa$_2$Cu$_3$O$_7$ coatings for large scale applications. © 1998 Published by Elsevier Science B.V. All rights reserved.

Keywords: Reduced oxygen; YBa$_2$Cu$_3$O$_7$; High rate evaporation; SrTiO$_3$; Critical current densities

1. Introduction

Recently, there have been demonstrations [1–3] of the production of meter long lengths of YBa$_2$Cu$_3$O$_7$ (YBCO) coated onto metallic tapes with a textured buffer layer. The feasibility of these tape conductors for construction of large devices such as power transmission lines and high field magnets appears promising. However, before this promise is realized, fabrication methods need to be developed to produce the tapes in sufficiently long lengths and at a commercially viable cost. A number of studies have been initiated to develop industrially scalable methods for the deposition of thick YBCO films [4,5] as well as for the fabrication of buffer layers and textured substrates [6,7]. Deposition techniques include pulsed laser ablation [1–3], electron beam (e-beam) evaporation [8–10] and the pyrolysis of metallo-organic films [11].

One of the methods being considered is the so-called BaF$_2$ post-deposition annealing process. In this process YBCO precursor films, having an approximate stoichiometric composition, are deposited onto substrates at or near room temperature. The precursor film is a fine mixture of BaF$_2$ and metallic

Y and Cu. [1] After deposition, the films are heated in a humidified atmosphere, at a reduced oxygen partial pressure to form textured $YBa_2Cu_3O_7$ films. An earlier detailed and extensive study [9,10] of the reaction of e-beam deposited precursor films has shown that good *c*-axis alignment and high critical current density, J_c, can be produced for YBCO films up to 1 μm thick using low oxygen partial pressure. The films are heated to 750–800°C at an oxygen partial pressure of ∼ 100–300 mTorr, in an atmosphere saturated with water vapor at ∼ 20 Torr [10]. Similarly, in a process involving precursor films deposited from metallo-organic compounds, it was also shown that *c*-axis aligned films could also be produced by heating the films under nearly identical conditions. However, in this study the thickness of the films was limited to a few hundred nanometers [11].

The evaporation of metals in commercial e-beam evaporation systems can be performed over large areas and at high rates making the e-beam deposition of precursor films a promising method for the fabrication of YBCO coated conductors. There are two important questions which needed to be addressed about this process in order for it to be commercially attractive: (1) how thick can the films be made while retaining *c*-axis alignment and (2) how fast can the precursor films be deposited? These concerns originate from the following: high field magnets and certain types of electrical devices for electric utilities require very high engineering superconducting current densities for the finished conductor. Thus, the anticipated thicknesses of the textured YBCO layers are ∼ 5 μm or greater. However, because *c*-axis YBCO films are known to grow from the interface between the precursor film and the $SrTiO_3$ substrate [11,12], it is not clear whether this mode of growth can be maintained for films 5 μm thick or greater. The maximum achievable thickness for this method needs to be determined. In addition, in earlier studies of e-beam deposited YBCO films via the BaF_2 post annealing method, the precursor films were deposited at slow rates, ∼ 1 nm/s, and thus it is also important to determine whether one can produce

similar high quality films using high deposition rates, e.g., > 10 nm/s. In order to answer these questions, we initiated a study of YBCO thick film fabrication by the BaF_2 process.

2. Experimental procedures

Precursor films of the approximate stoichiometric cation composition $Y_1B_2Cu_3$ were deposited on 3×10 mm² (100) $SrTiO_3$ substrates without external heating in a vacuum chamber. The Y and Cu metals were deposited using Temescal 14 kW e-beam guns and a custom 300 W thermal evaporation source was used to deposit BaF_2. Early in our study, it was found that the very high rate evaporation of BaF_2 by direct e-beam heating caused partial dissociation of the BaF_2 resulting in the presence of metallic barium in the precursor films. It is believed that the barium reacted with either atmospheric moisture or CO_2 after removal of the films from the vacuum chamber and prior to heat treatment.

The background pressure in the chamber was $1–2 \times 10^{-6}$ Torr during deposition. The vacuum chamber pumping system was oil-free using a cryopump for high vacuum and dry rotary vane pump and liquid nitrogen zeolite sorption pumps for roughing. The deposition rates of the individual sources were controlled by Inficon quartz crystal rate monitors. The reproducibility of the composition of the films was 5–10% from run to run. The composition was inferred from the calibrated deposition rates for each constituent, which was determined by the thickness measurements of Y, Cu, and BaF_2 films using a DekTak profilometer. Then this was confirmed by measuring compositions of selected films using Rutherford Back Scattering. The $SrTiO_3$ substrates were specified to be cut with misalignment of less than 0.2° with respect to [100] direction but a limited number of experiments were performed on miscut $SrTiO_3$ substrates. Prior to deposition the substrates were annealed at 1000°C in air for 2 h [9]. The properties of the films reported here are primarily for 3 μm thick films deposited at ∼ 10 nm/s. We have also prepared ∼ 1.5 μm thick films and the results from these films are compared with ∼ 3 μm thick films where appropriate. One of the concerns with

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[1] This was determined by transmission microscopy. Unpublished.

very high rate depositions is that the density of the precursor films may decrease with increasing deposition rate and affect the quality of the finished films. In order to examine this, a number of films were deposited with various deposition rates, 3–10 nm/s. The thickness of the films was measured before and after annealing. It was found that the reduction in the thickness of the films was less than 10% for all of the films deposited in this range of rates. In addition, no significant changes in superconducting properties were noted among these films.

The annealing station for the precursor films consisted of a furnace with a quartz tube connected to a manifold fitted with two electronic mass flow controllers. The reaction atmosphere was produced by mixing gases from two cylinders, one containing pure N_2 and the other a 0.11% O_2 + 99.9% N_2 mixture. The O_2–N_2 ratios were preset by combining the appropriate gas flows from the mass flow controllers and a constant total gas flow, 100 sccm, was used in all of the experiments. The gas mixture was saturated with water vapor in a glass bubbler before entering the quartz tube. The actual water vapor pressure was not determined, but was assumed to be equal to the vapor pressure of water at 25°C, i.e., ∼ 20 Torr. The gasses exited the heated quartz tube at atmospheric pressure and the oxygen content of the exit gas was checked with an Ametek Model TM-1B oxygen analyzer.

For the present study, the precursor films were annealed at three temperatures: 725°C for 13 h at 100 mTorr of oxygen partial pressure, 750°C for 8 h at 100 mTorr, and 800°C for 4 h at 300 mTorr. These values of temperature and oxygen partial pressure are in the range of conditions indicated in the phase diagram [10] for the synthesis of c-axis films. Although all of the experiments reported here utilized a water vapor pressure of ∼ 20 Torr, a cursory examination of the effect of the water vapor partial pressure on the growth rate of textured YBCO films was performed. Increases in water vapor partial pressure were obtained by heating the bubbler. Preliminary results indicate that the water vapor pressure, to a great extent, determines the growth speed of textured YBCO films and by extension the time needed to completely process the films. Higher water vapor pressures promote faster film growth and suppresses a-axis nucleation perpendicular to the substrate, but

the correlation of water vapor pressure with respect to critical current remains to be established.

The characterization routine for the films included θ–2θ X-ray diffraction, (XRD) and resistive measurement of the superconducting critical temperature, T_c. For critical current measurements, I_c, a standard four probe contact geometry was used with a distance of 3 mm between potential leads. The angular dependence of I_c with respect to the field orientation and the dependence of I_c with applied magnetic field were measured up to 1.1 T at 77 K in an electromagnet immersed in liquid nitrogen. Since the critical currents of the films were measured directly on 3 mm wide films without fabricating small bridges, the critical currents became too high, > 45 A, preventing the measurement of the self field of these thick films. The criteria for I_c was 1 μV/cm. In order to determine the critical current densities, J_c, the substrates were cracked in half and the thickness of the films was measured from cross sectional scanning electron microphotographs.

3. Result and discussion

An XRD spectrum for a 3 μm thick film annealed at 725°C is shown in Fig. 1. The textured YBCO is highly c-axis aligned with minor inclusions of a-axis oriented regions. The oxygen pressure, 100 mTorr, was essentially optimal for this temperature since higher oxygen pressures resulted in considerably enhanced a-axis phase growth, while anneals at lower
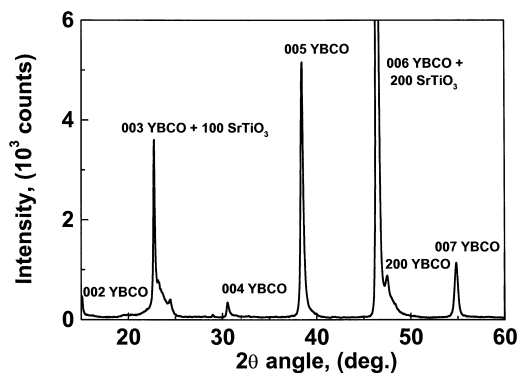

Fig. 1. XRD spectrum of 3 μm YBCO film annealed at 750 C in 100 mTorr partial oxygen pressure.
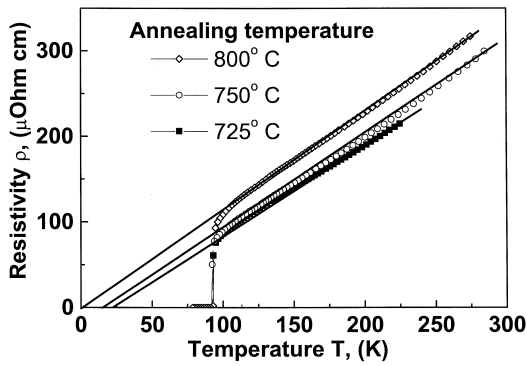
Fig. 2. Temperature dependence of the DC resistivity of 3 μm YBCO films annealed at 725, 750, 800°C temperatures. The lines present linear approximations of the $R(T)$ curve for $T < T_c$.

oxygen pressures produce films with inferior superconducting parameters. Similar results were also observed for other films annealed at 750 and 800°C with an oxygen partial pressure of 100 and 300 mTorr, respectively. In addition to the strong (00l) and weak (h00) YBCO reflections, we also observed very weak peaks identified as $BaCuO_2$, which was present in the matrix as well as on the surface of the film. This is believed to be due to the films having a higher Ba content than the stoichiometric composition. The critical currents of the films were strongly correlated with the amount of a-axis material. This was quantified by comparing the ratio of the (007) and (200) peak intensities in the XRD spectrum. The

absence of weak-link behavior, identified with $J_c > 10^5 \, A/cm^2$ at 1 T and 77 K and extrapolation of the resistivity vs. temperature curves to the origin, is observed for (007)/(200) peak ratios greater than 5 (see Fig. 2). In this case the critical current is limited by the flux pinning and not by high-angle boundaries. The temperature dependent resistivity, $R(T)$, is shown for three films in Fig. 2. The films exhibited good superconducting properties with T_c in the range 88–89 K and $\Delta T_c = 0.2$ K. The resistivity ratio $R(300 \, K)/R(100 \, K)$ varied form 2.9 to 3.5 and the room temperature resistivity 350 to 280 $\mu\Omega$ cm for the films annealed at 800 to 725°C, respectively, indicating that the films are of good quality. Fig. 3a compares critical current densities of 3 μm thick films vs. applied magnetic field. The films were annealed at 725, 750 and 800°C in an oxygen partial pressure of 100, 100 and 300 mTorr, respectively. The magnetic field was normal to the film ($H \| c$). As shown in the figure, the critical current density is greatest for the film reacted at 725°C. Since the resistivities, $R(T)$, of these samples were essentially the same, the higher value of J_c for the 725°C film may be related to an increased density of small defects for pinning vortices. It is generally believed that lower reaction temperatures tend to produce films with more growth defects.

The angular dependence of the critical current densities, $J_c(\theta)$, at 1 T for the films in Fig. 3a is presented in b. Here, θ is the angle between the
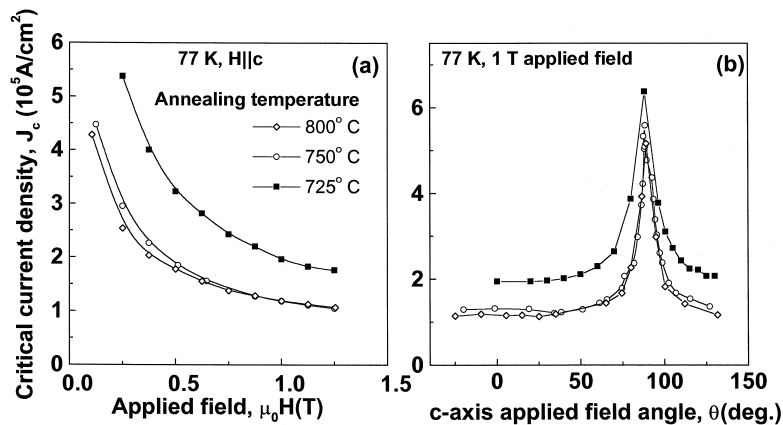

Fig. 3. (a) Critical current field and (b) angular dependences for 3 μm YBCO films annealed at 725, 750, 800°C. The lines are guides for the eye.

normal of the film and the applied field direction. The $J_c(\theta)$ curves exhibit a dramatic increase as the direction of the magnetic field becomes parallel to the substrate. This behavior is common to most high T_c superconducting films on single-crystalline substrates [13] and also was observed in 'thick' YBCO films on flexible metallic tapes [14]. Also, from the fact that the angular dependence of the critical current did not exhibit a peak at $c \| H$, it is concluded that twin boundaries do not play significant roles in determining J_c for these films.

We also wanted to examine the sensitivity of J_c with respect to the miscut of the substrates from the (100) substrate plane. Films 1.5 μm thick were deposited on miscut SrTiO$_3$ substrates. The substrates were miscut by 0, 0.5 and 1.0° with respect to the SrTiO$_3$ [100] direction. These films were processed under the same conditions i.e., an 8 h anneal at 750°C and 100 mTorr oxygen partial pressure. The critical current density, J_c, vs. θ, for the films is shown in Fig. 4. A 40% increase in J_c is observed as the miscut angle is increased from 0 to 1° and the effect is most pronounced when the applied magnetic field is aligned to the plane of the films. For $H \| c$ the increase was $\sim 30\%$.

The most important variable in this study for achieving high J_c values is the annealing temperature. Lower annealing temperatures are expected to result in films with a more defective crystalline structure which we believe enhances pinning. As an example, thick YBCO films grown by liquid-phase

epitaxy on various substrates in temperature range 950–1000°C [4] show excellent crystallinity but exhibit critical currents an order of magnitude less than for in situ and ex situ films grown in the temperature range 700–800°C [3,9,13]. The distribution and type of defects in post deposition annealed YBCO films are not known at present. Even the origin of the pinning centers responsible for the high critical currents in epitaxial YBCO films still remains controversial. For in situ deposition and film growth it is known that the films exhibit two types of growth, which can be described as a three-dimensional spiral or a two dimensional ledge-type of growth [13]. As the growing islands merge low-angle boundaries with a high density of edge dislocations occur at the boundaries. However, preliminary cross sectional TEM studies of these present films [1] have not revealed low angle grain boundaries in sufficient density, and it is not clear what are the pinning centers providing high J_c in these films.

Lower crystallization temperatures tend to produce more efficient pinning in films deposited in situ owing to the decrease in the surface mobility of the atoms. However, this can also cause degradation of T_c due to excess disorder, possibly cationic disorder and results in a lower limit for the substrate temperature. A similar mechanism seems to be responsible for higher J_c of ex situ films, annealed at low temperatures. Though, in the case of ex situ process, besides the possible cationic disorder, increased tendency for a-axis film growth at temperatures below 720°C sets a lower limit for stable c-axis oriented growth. So far we have not succeeded in growing completely c-axis oriented 3 μm thick films below 725°C.

The surfaces of miscut and vicinal SrTiO$_3$ form an ordered step-wise structure after high temperature annealing [15]. The structure consists of SrTiO$_3$ unit cell steps which promote c-axis phase nucleation for YBCO films grown ex situ [16]. The growing YBCO islands coalesce and can produce anti-phase boundaries, which in turn dissociate into stacking faults, as the film grows thicker. Stacking faults are potentially strong two-dimensional pinning sites. However, in this study, stacking faults were only seen for films with long annealing periods, on the order of 30 h. These films contained Y$_2$O$_3$ precipitates as well as stacking faults, which appear in conjunction with the
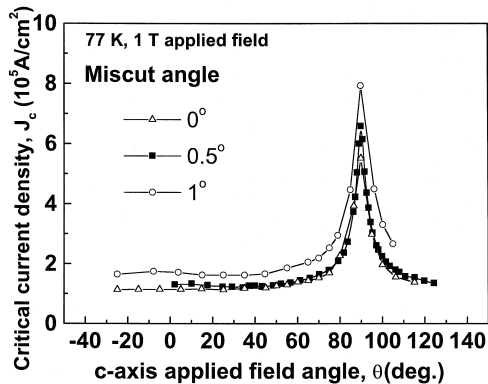

Fig. 4. Comparison of the angular dependences of the J_c for 1.5 μm YBCO films deposited on YBCO substrates miscut at 0, 0.5 and 1° relative to (100) plane. The lines are guides for the eye.

decomposition of the YBCO and might serve as pinning centers.

4. Conclusion

Using a combined method of e-beam and thermal evaporation, high quality c-axis aligned YBCO films, up to ~ 3 μm thick, were grown on (100) SrTiO$_3$ substrates. The films were deposited at deposition rates in excess of 10 nm/s using e-beam guns for Y and Cu and a thermal source for BaF$_2$. The films were post deposition annealed in a low partial pressure of oxygen saturated with water vapor. Critical currents well in excess of 1×10^5 A/cm^2 in fields of 1 T ($H\|c$) were measured. Lower annealing temperatures correlated with increased J_c and the highest critical currents were obtained at 725°C. Lowering annealing temperatures, further, resulted in excessive amounts of a-axis material and a decrease in J_c. These results show that the BaF$_2$ post-deposition annealing process for fabricating thick YBCO films is a strong candidate for the production of long tapes for large scale applications.

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